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AFRL-SR-AR-TR-04-

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1. REPORT DATE (DD-MM-YYYY) 31		2. REPORT TYPE Final		3. DATES COVERED (From - To) From 15-12-2000 to 14-12-2003	
4. TITLE AND SUBTITLE Predissociation and Quenching Dynamics of Electronically Excited Hydroxyl Radicals				5a. CONTRACT NUMBER F49620-01-1-0095	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Marsha I. Lester				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry University of Pennsylvania Philadelphia, PA 19104-6323				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Dr. Michael R. Berman AFOSR/NL 4015 Wilson Blvd., Rm 713 Arlington, VA 22203-1954				10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Unlimited Approve for Public Release: Distribution Unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT A series of studies have been conducted to examine the sources and sinks of electronically excited hydroxyl radicals via photon-assisted, unimolecular, and collision-induced processes. Significant progress has been made on three different fronts: (1) Simulation of ultraviolet emission data from the Space Shuttle's thruster plume as originating from solar-induced and collision-induced electronic excitation of hydroxyl radicals; (2) Detection of hydroxyl radicals in various vibrational levels of the ground electronic state through photoionization via high-lying Rydberg states; and (3) Examination of the photodissociation dynamics of highly vibrationally excited hydroxyl radicals at specific ultraviolet wavelengths (243 and 226 nm).					
15. SUBJECT TERMS Hydroxyl radicals, electronic predissociation, reactive quenching, nonadiabatic dynamics					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 7	19a. NAME OF RESPONSIBLE PERSON
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U			19b. TELEPHONE NUMBER (include area code)

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

20040617 058

AFOSR Final Report

F49620-01-1-0095

Predissociation and Quenching Dynamics of Electronically Excited Hydroxyl Radicals

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31 May, 2004

Objectives

A series of laboratory experiments have been carried out to examine the decay dynamics of electronically excited hydroxyl radicals via unimolecular and collision-induced processes. The goal of these experiments is to elucidate the mechanism for nonadiabatic processes that transform electronically excited $\text{OH } A^2\Sigma^+$ radicals into ground state oxygen $\text{O } (^3\text{P})$ atoms. In this grant period, the research program has focused on three main activities: (1) Simulation of $\text{OH } A^2\Sigma^+ - X^2\Pi$ emission data acquired from the Space Shuttle's thruster plume; (2) Detection of $\text{OH } X^2\Pi(v)$ through photoionization via the $D^2\Sigma^-$ and $3^2\Sigma^-$ Rydberg states; and (3) Examination of the photodissociation dynamics of $\text{OH } X^2\Pi(v)$ radicals in the vicinity of 243 and 226 nm. This research aims to address the role of nonadiabatic interactions in fundamental chemical processes, revealing the dynamical signatures associated with curve crossings and conical intersections between two or more potential energy surfaces. This study is of direct AFOSR relevance as the *reverse* chemical reaction, $\text{O } (^3\text{P}) + \text{H}_2\text{O} \rightarrow \text{OH } A^2\Sigma^+ + \text{OH}$ and $\text{O } (^3\text{P}) + \text{CH}_4 \rightarrow \text{OH } A^2\Sigma^+ + \text{CH}_3$, are possible sources of the $\text{OH } A \rightarrow X$ emission from the Space Shuttle's thruster plume. These laboratory measurements are needed to understand the chemical excitation pathways that lead to electronically excited $\text{OH } A^2\Sigma^+$ radicals in the interaction of the spacecraft's exhaust plume with the atomic oxygen atmosphere at orbital altitudes.

Accomplishments

This section summarizes our accomplishments during the past three years of AFOSR funding, December 15, 2000 through December 14, 2003. In this period, we have made

significant progress on three different fronts: (1) Simulation of OH $A^2\Sigma^+ - X^2\Pi$ emission data acquired from the Space Shuttle's thruster plume; (2) Detection of OH $X^2\Pi$ (v) through photoionization via the $D^2\Sigma^-$ and $3^2\Sigma^-$ Rydberg states; and (3) Examination of the photodissociation dynamics of OH $X^2\Pi$ (v) radicals in the vicinity of 243 and 226 nm.

My group carried out initial spectral simulations of the OH $A-X$ emission observed from the Space Shuttle's thruster plume, and later worked closely with Larry Bernstein, Yu-Hui Chiu, and Rainer Dressler on more comprehensive modeling of this system.¹ My group analyzed the $\Delta v=0$ bands (0-0, 1-1, and 2-2) in the OH $A-X$ emission spectra from numerous individual data sets using the LIFBASE program (free shareware, url: www.sri.com/cem/lifbase) to perform these simulations. We extracted vibrational populations for OH $A^2\Sigma^+$ ($v'=0-2$), rotational temperatures for each vibrational state, and integrated band intensities. Our spectral analysis indicated that several different processes contributed to the emission spectra to varying degrees under day and night solar illumination conditions with the exhaust plume directed into or perpendicular to the exhaust plume. This led to more comprehensive data mining and modeling by colleagues at Hanscom AFB, who identified the following sources of OH $A^2\Sigma^+$: (1) Solar-induced excitation of OH $X^2\Pi$ in the exhaust flow that yields rotationally cold OH $A^2\Sigma^+$. (2) Solar-induced photodissociation of H₂O in the exhaust at Lyman- α and further UV wavelengths that produces significant vibrational and rotational excitation of OH $A^2\Sigma^+$.² (3) Chemical reaction between atmospheric atomic oxygen and H₂O in the exhaust via $O(^3P) + H_2O \rightarrow OH A^2\Sigma^+ + OH X^2\Pi$. Process (3) can only be seen clearly under nighttime conditions with the exhaust plume directed into the atmospheric wind. The OH $A-X$ emission signal from process (3) is substantially weaker than that observed under solar illumination conditions. Under conditions where the OH $A-X$ emission originates primarily from process (3), the OH $A^2\Sigma^+$ products were found mainly in $v'=0$ and 1 with a rotational temperature of 4,000 K. Electronic predissociation of OH $A^2\Sigma^+$ ($v' \geq 2$) limits the amount of electronically excited OH that can be detected by $A-X$ emission, which may result in underestimation of the cross section for the reactive process (3). This work has been published from the point of view of spacecraft contamination.¹

Since we have or will probe H (2S) and O (3P) atomic products from reactive quenching of OH $A^2\Sigma^+$ ($v=0$) + M, we spent some time exploring the interaction of the UV probe radiation

with OH radicals and, as a result, discovered some very interesting new spectroscopy and photodissociation dynamics of the OH radical. The H (2S) and O (3P) atoms are usually probed by two-photon laser-induced fluorescence or 2+1 REMPI at 243 nm and 226 nm, respectively. We found that two-photon excitation at these wavelengths takes OH into the vicinity of its lowest-lying Rydberg states ($D\ ^2\Sigma^-$ and $3\ ^2\Sigma^-$). We then recorded the first supersonic jet cooled spectra of OH/OD radicals by 2+1 REMPI via these Rydberg intermediate states. The supersonic expansion cools OH/OD to its lowest rovibrational level and greatly simplifies the REMPI bands to three strong lines, $Q_1(1)$, $R_1(1)$, and $S_1(1)$, as shown in Fig. 1. Time of flight detection is gated on the OH^+ or OD^+ mass, however, interference from strong H_2O transitions in this energy region can also appear.³ Nevertheless, these experimental conditions have allowed for the discovery of new, higher vibrational levels in each of the Rydberg states, specifically $D\ ^2\Sigma^-$ ($v=3$) and $3\ ^2\Sigma^-$ ($v=1$). With a H_2O/Ar discharge source, we have also observed hot band transitions (but still rotationally cold) originating from excited vibrational levels of the ground $X^2\Pi_{3/2}$ state, namely $v''=1, 2$, and 3 , to these Rydberg states. Spectroscopic constants characteristic of OH in these Rydberg states have been determined based on the rotational band structure in the REMPI spectra. These constants will be compared with previous experimental work of lower vibrational levels^{4,5} and theoretical predictions of two-photon transition probabilities via the $I\ ^2\Sigma^-$ repulsive state, which are based on new *ab initio* calculations of the potentials, in a comprehensive manuscript that is in preparation.⁶ With the recent publication of a 1+1' REMPI scheme to the $D\ ^2\Sigma^-$ ($v=0$) state,⁷ we are also computing the one-photon transition probabilities to the Rydberg states.

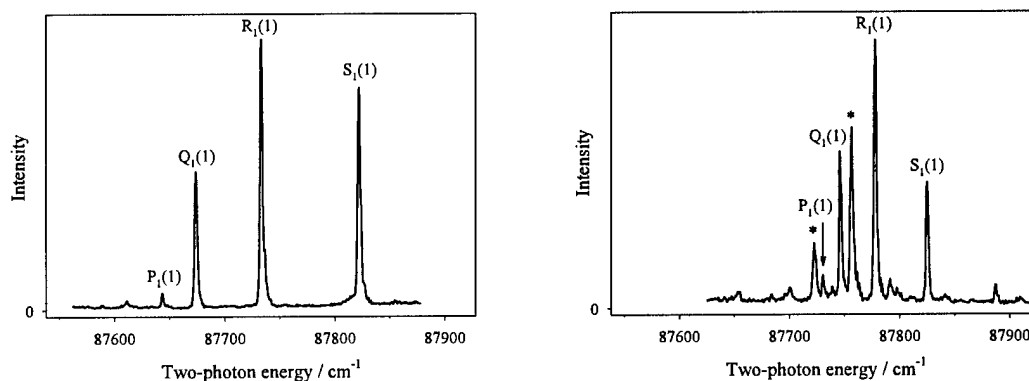


Fig. 1 Simplified 2+1 REMPI spectra of OH (left) and OD (right) radicals in the $3\ ^2\Sigma^- - X^2\Pi\ 0-0$ region achieved by supersonic cooling. The asterisks indicate overlapping H_2O lines.

We have also pursued a one-color photodissociation experiment on OH/D radicals with Dave Parker's group in Nijmegen using the velocity map imaging technique that he pioneered.^{8,9} We wanted to determine if the O(³P) probe radiation at 226 nm or H(²S) probe radiation at 243 nm would also photodissociate OH/D via a one- or two-photon process. The velocity map imaging technique is the best way to answer this question because we obtain information about the velocity and spatial anisotropy of the recoiling H(²S) or O(³P) fragments. Our initial results on OH showed a kinetic energy release of 0.12-0.14 eV to the O(³P) fragments (1/17 of the total kinetic energy release, TKER), which increased as expected upon deuteration (2/18 of the TKER). In addition, we learned that the OH/OD excitation was a perpendicular transition from the anisotropic spatial profile of the O-atom fragments.

We have since repeated these experiments using a hexapole field to focus and state-select the OH radicals in the gas pulse,^{10,11} rather than probing all components produced in the H₂O/Ar discharge source.¹² The hexapole state selects OH molecules with the $|M_J|=3/2$ component of the upper Λ -doublet level (f-symmetry) of the lowest rotational state of OH ($X^2\Pi_{3/2}$, $J=3/2$) and focuses these molecules to the point of laser interaction. The focusing is observed in 2+1 REMPI spectra as a eight-fold enhancement of the Q₁(1) and S₁(1) lines that originate from the selected ground state level. We then measured the angle-speed distribution for the O(³P₂) atom product following OD photodissociation at 226 nm and the D($n=1$, ²S) product for photodissociation at 243 nm. New, fully *ab initio* calculations of the lower electronically excited states of OD were also performed to yield accurate wavefunctions and internuclear dependent transition dipole functions for the states involved. These have been used to explain the observed dissociation dynamics.

Two rings appear in the raw O⁺ velocity map image (hexapole on – hexapole off) corresponding to O(³P₂) atoms with velocity of 1670 and 1755 m/s with an uncertainty of ± 25 m/s. Converting these O atom velocities to total kinetic energy release [TKER = (m_{OD}/m_D) \times KER_O] yields values of 2.10 and 2.39 ± 0.06 eV. For D⁺, at least three rings are seen, corresponding to D atom velocities of 11800, 12800, and 13800 m/s and TKER values of 1.62, 1.91, and 2.20 ± 0.06 eV, respectively. The TKER curves obtained from integrating over the angular distribution of the images are shown in Fig. 2.

The observed peaks in the TKER distributions can only be assigned to one-photon dissociation of OD in high vibrational levels of the ground ² Π electronic state. Using the energy

balance equation $\text{TKER} = h\nu + E(\text{vib})_{\text{OD}} - D_0$, the two main peaks seen for O atom detection at 226 nm are attributed to photodissociation of OD in $v = 3$ and $v = 4$, as marked in Fig. 2. For D atom detection at 243 nm, the three main peaks correspond to dissociation of OD ($v = 3, 4$, and 5).

Complementary first principle calculations also demonstrate that the photodissociation processes at 226 and 243 nm occur by one-photon excitation of OD $X^2\Pi(v)$ to the repulsive $1^2\Sigma^-$ state. The relative intensity of the peaks in the TKER curves of Fig. 2 can be qualitatively understood based on the photodissociation cross sections computed for various vibrational states. The calculations predict that at a vibrational temperature of $\sim 1700\text{K}$ the $v = 3$ and 4 states (and $v=2$ to a lesser extent) result in the largest photodissociation

yield at 226 nm, while a distribution of states about $v = 4$ (primarily $v = 3, 4$, and 5) contribute to the yield at 243 nm. The predicted yields are shown in the bar graphs of Fig. 2. An important conclusion from this work is that neither one-photon nor two-photon dissociation is detected from OD $X^2\Pi$ ($v=0, 1$) at 226 or 243 nm. This OD photodissociation study has been published as a rapid Communication.¹³

Equipment

The funds obtained through the DURIP grant (03/01/01 – 12/31/01) were used to purchase a high power ArF excimer laser and a time-of-flight mass spectrometer with associated vacuum system.

Personnel

This grant has partially supported the research of graduate students Margaret Greenslade, Eunice Li, and Bethany Pond. In addition, Maria Tsiouris, a postdoctoral researcher, has worked part-time on this project.

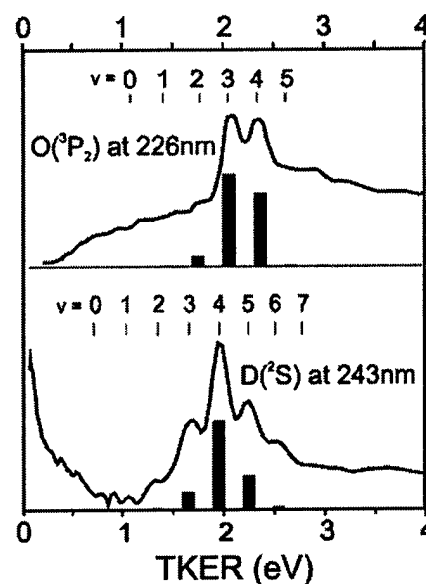


Fig. 2 Total kinetic energy release derived from velocity map images of $\text{O}(^3\text{P}_2)$ and $\text{D}(^2\text{S})$ fragments following photodissociation of OD at 226 and 243 nm. The bar graphs show the calculated photodissociation yields for OD $X^2\Pi(v)$ at a vibrational temperature of 1700K.

Interactions/Transitions

I have maintained close contact with David Yarkony (Johns Hopkins) through discussions at three meetings this past summer. He has worked on theoretical aspects of the OH $A^2\Sigma^+ + OH \rightarrow H_2O + O(^3P)$ reactive quenching problem. In addition, my group is collaborating with David Parker at Nijmegen (the Netherlands) on velocity map imaging studies of H (2S) and O (3P) products following photodissociation OH/D radicals at 243 and 226 nm, respectively. Finally, I have worked with Rainer Dressler and colleagues at Hanscom AFB on the analysis of OH emission data from the Space Shuttle's thruster plume.

Inventions and patent disclosures

There have been no inventions leading to patent disclosures during the period of this grant.

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